A Classification Scheme for Toroidal Molecules

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1 Introduction

The last decade witnessed the discovery of diverse hollow graphitic structures [1]. Several spherical [2] and cylindrical [3] structures have been observed. A natural question is whether structures with other topologies, such as tori, also occur. It is reasonable to expect that molecules that are multiply connected and have negative curvature (i.e. have regions that approximate a saddle) would have distinct physical and chemical properties. For example, certain quantum and transport phenomena depend on multiconnectivity [4], and it is

known that negative curvature has important consequences for the dynamics on the surface [5]. Toroidal molecules may have applications in host-guest chemistry [6], where the "hole" in the torus accomodates the "guest". It has also been suggested that toroidal molecules may have applications as components in nanotechnology [7] and as catalizers [8].

Structures with two concentric cylinders that inter-connect have been observed [8]. Gluing two of these objects together would make a torus. In the present study we shall focus on structures in the shape of a doughnut. Miscellaneous proposals for toroidal molecules have been suggested [7, 9, 10, 11, 12]. Ab initio calculations for the energetics and geometry of several toroidal carbon molecules have been performed in [13].

The purpose of the present study is to present a classification scheme for a wide class of toroidal molecules. This classification scheme can distinguish between toroidal isomers. For example, Table I shows two C_{120} and two C_{240} isomers of toroidal carbon that are resolved by our classification.

Our tool is a set of tiling rules [14], adapted to the description of non-crumpled toroidal molecules that approximate a surface of revolution. These tiling rules reflect the energy penalty for stretched bonds and deformed bond angles. Our method is amenable for computarized search (as the "orange-peel" method [15] in the case of spheroids). A tiling pattern is determined by

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four integer indices which characterize the basic "unit cell", which is repeated periodically to make a torus. The approximate positions of all the atoms in the molecule are determined by these four integers and by the number of unit cells in the torus. An announcement of some of the results in the present study is found in [16].

Although we do not claim that all stable toroidal molecules belong to the class of tilings that we introduce, this class contains most toroidal molecules proposed in the literature and is large enough to include close approximations to tori with prescribed reasonable dimensions.

As an application we describe results of a numerical study of the energetics of several toroidal carbon molecules. The study involved:

1. The relaxation of model carbon atoms represented by tiling to a stable molecular configuration, through minimization of the $\sigma-$bonds geometric potential energy. We have used a phenomenological potential due to Tersoff [17]. From here, average energies and binding energies of the least bound atoms were obtained.

2. HOMO-LUMO and other properties of the π-electrons in Hückel model.

The results (Table I) support the conjecture that many toroidal carbon molecules are stable configurations.

2   Tilings

We are interested in surfaces that approximate toroidal surfaces of revolution, as in Fig. 1. (This surface is known as the "anchor ring".) A point P on this surface has the cartesian representation

$$R\left\{\left(1 - \frac{\cos\theta}{\eta}\right)\cos\phi \ , \ \left(1 - \frac{\cos\theta}{\eta}\right)\sin\phi \ , \ \frac{\sin\theta}{\eta}\right\} \ , \tag{1}$$

where $\{\theta, \phi\}$ are the toroidal coordinates. The parameter $R > 0$ determines the size, and the parameter $\eta > 1$ determines the shape. (Large η corresponds to thin tori.) Eq. (1) induces the metric and area [18]

$$\eta^2 R^{-2} ds^2 = d\theta^2 + (d\phi)^2 \ (\eta - \cos\theta)^2 \ ;$$

$$\eta^2 R^{-2} dA = d\theta d\phi (\eta - \cos\theta) \ . \tag{2}$$

A toroidal surface may be represented by the rectangle $[0, 2\pi] \times [0, 2\pi]$ in the (θ,ϕ) plane. Opposite sides of this rectangle are identified (i. e., are understood as being the same line); this identification is equivalent to the periodicity of Eq. (1) in θ and ϕ. We shall refer to lines of fixed θ (resp. ϕ) as latitudes (resp. longitudes) and draw them horizontal (resp. vertical).

A toroidal carbon molecule can be represented by a graph on such a rectangle (like the solid lines in Fig. 2), where atoms sit at vertices and each vertex is trivalent. (Following the nomenclature of graphs theory, the *valence of a vertex* is the number of edges that meet at the vertex; if atoms sit at

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the vertices this is the same as the chemical valence.) Since carbon bonds prefer angles near 120°, graphs with pentagonal, hexagonal and heptagonal rings are favored and we allow only these.

It is known that pentagonal rings are associated with positive (Gaussian) curvature and heptagonal rings with negative curvature. Tori have positive curvature far from their axis (where their surface is locally similar to an ellipsoid) and negative curvature in the hub region (where the surface looks like a saddle). Therefore, noncrumpled toroidal molecules should contain pentagonal and heptagonal rings (in equal numbers by Euler's Theorem). The integrated Gaussian curvature of the torus in Fig. 1 for $-\pi/2 < \theta < \pi/2$ is -4π, and is cancelled by the integrated Gaussian curvature over the rest of the torus. Since the positive part is 4π, just like for the sphere, it suggests that the number of pentagons should be about twelve (and equal to the number of heptagons). Indeed, our numerical study shows that hexagons-only tori (e. g. [9]) have large energies; they have atoms that are strained about three or four times more than the most strained atoms in typical molecules that allow for pentagons and heptagons.

It will be useful to represent a molecule by its *dual graph*. The dual graph is constructed by drawing a vertex inside every face of the direct graph, and connecting vertices of faces with a common edge. The dual graph of Fig. 2

has been drawn with dashed lines. The duality operation exchanges faces (and their number of edges) with vertices (and their valence). Since we are considering trivalent atoms, and since we allow rings with 5, 6 and 7 atoms, the dual graph consists of triangles and has vertices of valences 5, 6 and 7. (The name "dual" reflects the fact that the dual of the dual is isomorphic the initial graph.)

We shall idealize the triangles in the dual graph and represent them by *tiles*: by this we mean that, instead of having all sorts of shapes, only a small family of triangles will be used as building blocks of our dual graphs. Our tiles will be right-angled isosceles triangles, as in Fig. 3; the motivation for this choice is given in the appendix. As discussed in the appendix, our set of tiles includes various sizes, reflecting the non uniform metric in the $\{\theta, \phi\}$ plane. (Large tiles are placed where $\cos \theta$ is large and vice versa.) It follows by Pythagoras that the different tiles are related by scaling by powers of $\sqrt{2}$. Due to the privileged role of latitudes and longitudes, we shall (initially) require that each tile have at least one side along one of these directions. More general structures will be discussed in Section 5.

Tiles will be classified by their sizes, and assigned a *generation number*. The largest tiles will be called the first generation and the tiles in the i-th generation are those with an area which is 2^{i-1} times smaller. In the first

generation we allow only the two orientations (related by a π rotation) with the hypotenuse along a latitudinal line as shown in Fig. 3a; this will be required from every odd generation. This turns out to give rise to an array of equidistand horizontal lines, a feature that agrees with metric (2), which depends on θ, but not on ϕ.

In the second generation we allow the four tiles in Fig. 3b. Tiles in generation $p+2$ are the same as those in generation p, except for scaling by a factor of $\frac{1}{2}$. Clearly, tiles that share a common edge differ by at most one generation. Since there is only one way of matching odd generation tiles, the tiling of an odd-generation region is uniquely determined by its border; on the other hand, since a square can be tiled in two ways (see Fig. 4), the tiling of an even-generation region involves a choice of orientation for each square.

We define the *length* $L(\theta)$ of a latitudinal line as the number of edges it contains. Our tiling rules have the property that $L(\theta)$ is larger when the line passes through high generation regions. In Fig. 5, $L(\theta)$ varies from 1 in the horizontal lines in the first generation to 3 in the third-fourth generation region. Likewise, we define the length of a longitudinal line as the number of horizontal lines it intersects. Our tiling rules ensure that the total length of longitudinal lines is independent of ϕ, as it should. This length will be dubbed the "girth" and denoted by g. We also define $g_i(\phi)$ as the

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length within the i-th generation regions. If a longitudinal line crosses several regions of the same generation i, then $g_i(\phi)$ is defined as the *total* length across all these regions. In Fig. 5, $g_1 = g_3 = 2$ and $g_2 = g_4 = 1$ (independent of ϕ). Denoting by m the number of generations in the tiling, $\sum_{i=1}^{m} g_i(\phi) = g$.

Since the linear dimension of the last generation is smaller than that of the first by a factor $2^{(m-1)/2}$, and since the first generation has the hypotenuse along a latitudinal line (while the last generation has this property only if m is odd, introducing an additional factor $2^{1/2}$ in the counting metric along the latitudinal direction when m is even), Eq. (2) can be used to relate η to the number of generations m:

$$\frac{\eta + 1}{\eta - 1} \sim 2^{[m/2]} \; , \tag{3}$$

where $[m/2]$ = integral part of $m/2$. Therefore, the number of generations plays a role analogous to $1/\eta$. A cylinder can be built with one generation, skinny tori are associated with first and second generation tiles and, the fatter the torus, the more generations are needed.

Unlike the sphere, which is unique up to scaling, the tori of Eq. (1) depend also on the shape parameter η. *A priori*, it is not clear whether this family has a distinguished member. It turns out that the case $\eta = \sqrt{2}$ is special. In the theory of surfaces the torus of revolution with $\eta = \sqrt{2}$ is

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known as the Clifford torus and is distinguished by being the minimizer of the Willmore functional, i. e., it minimizes the square of the mean curvature [19]. The fattest torus we shall study has five generations, and is inspired by the Clifford torus. As we shall see, it does have marked stability. For fatter tori, $\eta < \sqrt{2}$, axially symmetric structures are disfavored [19].

As mentioned above, valence plays the role of curvature: valence 5 (resp. 6, 7) vertices carry positive (resp. zero, negative) curvature. Since curvature also implies non-constant metric, we want no 5 and 7 valence vertices embedded in single generation regions, where all triangles have the same Euclidean area. The pair of tiles of the odd generations have indeed this behavior built into them: only sixfold vertices can be made with them alone. On the other hand, Fig. 4 shows a tiling by even generation tiles with valences 5 and 7. These pentagon-heptagon pairs do not produce curvature of the form required by metric (2); they merely produce crumpling, and their integrated effect within a single generation region is zero. Therefore, pentagons or heptagons will be allowed only at the interfaces between different generations.

The predominance of pentagons over heptagons is the discrete analog of the (Gaussian) curvature. In our case, it should be a decreasing function of $\cos\theta$ and, also, of the size of the tile. Therefore, the predominance of pen-

tagons over heptagons ought to be an increasing function of the generation number. However, since every pentagon-heptagon pair necessarily involves angles that differ from 120°, we shall attempt to include as few of them as reasonable. Moreover, we shall deal only with small numbers of generations (≤ 5), so that it seems reasonable to compromise the smoothness of the curvature on behalf of limited numbers of pentagons and heptagons, and locate them only where they are most required. In summary, we impose the following:

5-6-7 Rule: For a torus with m generations, all the heptagons lie at the interfaces between the 1st and the 2nd generation and all the pentagons lie at the interfaces between the m-th and the $(m-1)$-th generation. (If there are only two generations, both the heptagons and the pentagons lie at the interfaces between them.) Furthermore, we require that around every heptagon (resp. pentagon) there be a majority of tiles of generation 1 (resp. m).

Figs. 5-7 are examples of tilings which obey the 5-6-7 rule.

3 Skeletons and Relationships

Given a set of interfaces between generations, the position of each tile in the tiling is determined uniquely by the 5-6-7 rule (although not for every set of interfaces does a legal tiling exist). The set of interfaces will be called the *skeleton*. The $(2p-1,\ 2p)$ interfaces are zigzag lines (e.g. Fig. 8a) and the $(2p,\ 2p+1)$ interfaces are horizontal lines (e.g. Fig. 8b). Therefore, regions that contain $2p-1$ and $2p$ tiles lie within a horizontal stripe, which will be called a *p-th stripe*. (If there are only 2 generations, there is just one stripe; if the number m of generations is odd, then the last stripe has tiles of the m-th generation only.) Figs. 6 and 7 have one stripe; Fig. 5 has two.

Since according to metric (2) the length of the latitudinal lines has only one minimum and one maximum, we require that the regions of generation i, $1 \leq i \leq m$, be located in monotonic and consecutive order, both when going from region 1 to m by increasing or by decreasing θ. The 5-6-7 rule imposes a strong constraint on the class of possible skeletons with two or more stripes: all the zigzag interfaces are parallel to each other and, with the exception of the pentagonal and possibly the heptagonal vertices, the vertices of the zigzag interfaces lie at the stripe borders (see Fig. 9). This has two consequences: First, the tiling has mirrors of symmetry at the longitudinal (vertical) lines that contain the pentagons and the heptagons; it also has centers of inversion

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that lie midway between the heptagons (resp. pentagons) which are located at different zigzag lines (keeping periodicity in mind). Second, the g_i's are independent of ϕ, in agreement with the our target metric (2). If the skeleton consists of just one stripe, then the symmetry, the constancy of the g_i's and the zigging between two lines of constant latitude don't follow from the 5-6-7 rule (e. g. Figs. 10-11), but we impose them in order to mimic the symmetry properties of metric (2). The independence of the g_i's on ϕ rules out the tori considered in Refs. [10, 11], which are cylindrical tubes connected by elbows.

We are thus left with a class of tilings such that the skeleton (and the entire tiling) is completely determined by four numbers (see Fig. 9): m (the number of generations), g_1 and g_m (the contributions of the first and last generation to the girth), and z (the number of edges in a zig of the (1,2) interface). For a generation number i which is odd, g_i must be even. If $i \neq 1, m$, then $g_i = 2^{p-1}z$, where p is the number of the stripe.

The girth of the torus is given by

$$g = g_1 + g_{\mathrm{mid}} + g_{\mathrm{end}} + g_m \ , \tag{4a}$$

with

$$g_{\mathrm{mid}} = \begin{cases} 0 & m \leq 2 \\ z & 2 < m < 5 \\ (2^k - 3)z & m \geq 5 \end{cases} \tag{4b}$$

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where $k = [(m + 1)/2]$ is the number of stripes ([ ] denotes integral part), and

$$g_{\text{end}} = \begin{cases} 2^{k-1}z & m \text{ even and} \geq 4 \\ 0 & \text{otherwise} \end{cases} \tag{4c}$$

The ϕ-range spanned by a zig and a zag will be called a *unit cell*. The number of atoms in a unit cell is given by

$$A = \begin{cases} 2z\left(g_1 + 2^{[m/2]}g_m\right) & m < 3 \\ 2z\left(g_1 + 2^{[m/2]}g_m + (2^{m-1} - 2)z\right) & m \geq 3 \end{cases} \tag{5}$$

The length of the shortest latitudinal line in a unit cell is given by

$$L_{\text{min}} = 2z - \text{Min}(g_1, z) . \tag{6}$$

The length of the longest latitudinal line in a unit cell is

$$L_{\text{max}} = \begin{cases} 2^{k-1}z & m \text{ odd} \\ 2^{k-1}z + \text{Min}(g_m, 2^{k-1}z) & m \text{ even} \end{cases} \tag{7}$$

A unit cell contains 2 pentagons and 2 heptagons.

4   From Tiles to Tori

We build a torus in three dimensional space from a latitudinal array of n unit cells. By associating periodic coordinates $\{\theta, \phi\}$ to the tiling plane, the

three-dimensional positions follow by Eq. (1). The line $\theta = 0$ is assigned to the horizontal line through the centers of inversion near the vertices of valence 7 (such as the "X" in Fig. 5) and the horizontal line $\theta = \pi$ passes through the centers of inversion near the vertices of valence 5 (such as the asterisk). We then increase (resp. decrease) θ by $2\pi/g$ when going up (resp. down) by one horizontal line. ϕ is assigned by requiring it to span 2π in the periodic tiling and to be linear along the horizontal planar distance in the tiling plane. Finally, we impose periodicity $\{\theta+2\pi, \phi\} \equiv \{\theta, \phi+2\pi\} \equiv \{\theta, \phi\}$. For example, for the molecule obtained by 5 repetitions of the unit cell shown in Fig. 5, if the longitude $\phi = 0$ is chosen to pass through the "X" and the asterisk, the coordinates of the center of the disk (located at $\frac{1}{3}$ of the height of the triangle) would be $\{\theta = 19\pi/18, \phi = -\pi/10\}$.

From the symmetry of the tiling, discussed in the previous section, it follows that a torus with n unit cells has symmetry D_{nd}, which is the highest symmetry of a torus in three dimensions that could be expected from a discrete construction.

The number of unit cells in the molecule may be estimated a priori by comparing the difference in the perimeters at $\theta = 0$ and $\theta = \pi$ to that of a geometric torus. This gives

$$n \sim n_0 = 2g/(L_{\max} - L_{\min}) \,, \tag{8}$$

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where g, $L_{\max}$ and $L_{\min}$ are given by (4), (6) and (7).

To evaluate the parameters R and η which appear in Eq. (1), R (resp. R/η) is taken proportional to the average latitudinal (resp. longitudinal) length, and the constant of proportionality is a "material parameter". For carbon atoms, appropriate values are

$$R = 0.2n(L_{\min} + L_{\max})\text{Å} \tag{9}$$

and

$$R/\eta = 0.4g\text{Å} . \tag{10}$$

(The geometric data in Table I do not follow directly from Eqs. (9) and (10); they were obtained after refinement through minimization of the interatomic potential.)

The present section suffices to deal with most molecules considered in this paper. Section 5 provides generalizations, and may be skipped on first reading.

5   Associated Tilings

Each of the tilings of the previous sections can be used to generate several descendent structures. These are more general than those considered so far

and in some cases involve tiles of different shapes. The generalizations we consider are Goldberg inclusion, elongation, chirality and torsion.

Inclusion consists of drawing v vertices inside each tile and then connecting both the old and the new vertices to form a new array of triangles in the dual graph. Vertices on the edge between two tiles are counted as $\frac{1}{2}$ in each. This procedure increases the number of atoms by a factor $q = 1 + 2v$. Connections are made so that old vertices retain their valences, new vertices have valence 6, and nearest vertices are connected. We restrict ourselves to the cases in which this rule for the connection of the vertices is unambiguous. If $q = 1 + 2v$ is of the form

$$q = \ell_1^2 + \ell_2^2 + \ell_1\ell_2 , \tag{11a}$$

with ℓ_1 and ℓ_2 integers, then a distribution of vertices for which connections are unambiguous is obtained by a variation of the *Goldberg transformation* [20]: using local coordinates for each tile, such that its vertices are at $(x = 0, y = 0)$, $(x = 1, y = 0)$ and $(x = 0, y = 1)$ (with $\hat{\mathbf{x}}$ to the right of $\hat{\mathbf{y}}$), the included vertices are at

$$
\begin{aligned}
x &= (n_1(\ell_1 + \ell_2) + n_2\ell_2)/q , \\
y &= (-n_1\ell_2 + n_2\ell_1)/q ,
\end{aligned}
\tag{11b}
$$

where (n_1, n_2) are integers such that (x, y) lies inside the tile. Fig. 12 shows the Goldberg transformation $(\ell_1, \ell_2) = (1, 2)$ applied to the tiling $g_1 = 2$, $g_2 =$

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$z = 1$.

Inclusion generates a family of molecules for which the number of pentagons and heptagons and their relative positions (and therefore the overall shape) remain fixed. Except for the cases $\ell_1 = \ell_2$ and ℓ_1 or $\ell_2 = 0$, which are considered below, the Goldberg inclusion gives rise to chiral molecules.

A Goldberg inclusion with indices $(\ell_1, \ell_2) = (\ell, 0)$ (or $(0, \ell)$) will be called *inflation*. Inflation is the discrete analog of scaling. Inflation by a factor ℓ replaces all the tiles by "super-tiles" where each new tile is made of ℓ^2 scaled copies of the old tile (or its π rotated image). Inflation preserves the generation number, increasing by the factor ℓ^2 the number of atoms in each. Inflation by a factor ℓ gives a tiling within the class we have considered, leaving m and n unchanged, while leading to multiplication of z and all the g_i's by ℓ. Therefore, for classification purposes it is convenient to consider primitive tiling, i.e. sets of numbers (g_1, g_m, z) which have no common divisor. (Except possibly 2, since g_i must be even for odd i.)

A Goldberg inclusion with indices $\ell_1 = \ell_2 = 1$ is a *leapfrog* [21]. In three dimensional space, the leapfrog operation is a vertex truncation through the mid-points of the edges, so that every old vertex turns into a hexagon and the number of atoms is multiplied by 3. Leapfrogged structures are guaranteed to have closed shells in the Hückel spectrum [22]. The effect of leapfrogging

twice is the same as that of inflation by a factor 3.

The tori of Ref. [10] may be obtained by *elongation*. Elongation is defined for tilings with two generations. It consists of cutting the tiling along an approximately longitudinal line (following the edges of the tiles), separating the two pieces by an integer latitudinal distance, and filling in with tiles of generation 2, in such a way that all additional vertices are hexagonal. Fig. 10 shows an elongation of the tiling $g_1 = 2$, $g_2 = z = 1$.

The tori considered by Dunlap [11] have tilings which typically look like that in Fig. 13, and do not obey the 5-6-7 rule. These tori have D_{nh} rather than D_{nd} symmetry. Their curvature does not vary smoothly as in metric (2); it concentrates at the defects.

For many tilings there exist latitudinal lines $\theta = \theta^*$ which are embedded in a single odd generation (first or last, with $L(\theta^*) \equiv L^*$ equal to either $nL_{\min}$ or $nL_{\max}$). If this is the case, manifest *chirality* [23] may be introduced by using θ in the range $\theta^* \leq \theta < \theta^* + 2\pi$ and associating to the coordinates $\{\theta, \phi\}$ in the tiling the coordinates $\{\theta, \phi + j\theta/L^*\}$ in three dimensional space, with j integer. (This is the analog of Dehn twist in the theory of Riemann surfaces.) This amounts to identification of the edge at $\theta = \theta^*$ with the edge at $\theta = \theta^* + 2\pi$ shifted by j. The 5-6-7 rule will still be fulfilled. Unless $|j| << L^*$ and $|j| << g$, this shift produces considerable strain. It is possible

to construct tori with g_1 odd or with m odd and g_m odd, provided that we introduce a chiral shift by a half-integer j.

Shifts in the longitudinal boundaries of the tiling would lead in general to a misfit in the skeleton. However, if there are only two generations, *torsion* can be introduced by drawing zigs (z_1) longer than the zags (z_2), as in Fig. 11. The resulting molecule is an open helix rather than a torus. The sinus of its pitch angle may be estimated as $2(z_1 - z_2)/(L_{\max} - L_{\min})$. Helical structures have been studied in [24].

Let us mention that better approximations to metric (2) can be achieved by two-generation tilings in which the skeleton consists of two parallel jagged lines, such that the number of heptagons minus the number of pentagons in the range $[0, \theta]$ is approximately proportional to $|\sin \theta|$. Tilings like this would have a very large number of atoms per unit cell and, also, a very large n_0 in Eq. (8).

6   Energetics

For each molecule, we calculate two complementary phenomenological contributions to the energy. The geometric contribution is calculated by means of an interatomic potential, and the contribution of delocalized electrons by means of Hückel model.

Interatomic Potential: We use Tersoff's potential [17].

The tiling rules of the previous sections not only describe the connectivity of the molecule, but also suggest values for n, R and η through Eqs. (8)-(10). The carbon atoms (located at the centers of each triangle), are assigned initial positions in space which correspond to their toroidal coordinates. The positions of all the atoms are then allowed to vary in three-dimensional space to minimize the total potential energy of the bonds. Good tilings flow to a nearby local minimum. Uncontrolled guesses for the initial coordinates result in atoms being lost to infinity.

We have used Powell's method [25] to flow to a local minimum of the molecular energy. In all cases, our tilings provided initial guesses for the atomic positions within the basin of convergence of the minimization algorithm. When the number of coordinates is large, analytic expressions for the derivatives of the energy must be supplied in order to obtain reliable minima.

For every tiling, we tried several values for the number n of unit cells. For the tilings considered, the largest binding energies of the entire molecule were usually obtained for $n = 6$ and the largest binding energy of the most strained atoms, for $n = 5$. The results are shown in Table I. Since the differences between $n = 5$ and $n = 6$ are small, we present the results for $n = 5$ only. To facilitate comparison, Tersoff's energies are given relative to

that of an ideal graphitic plane, which is -7.40 eV per atom. It is instructive to compare these energies with those of a torus with girth 4 and 160 atoms, but with hexagonal rings only: in this case $N(\bar{E} - E_G)/|E_G| = 29$ and $10^3(E_{\text{worst}} - E_G)/|E_G| = 411$ (and strain increases for larger girth).

Hückel Model: Hückel's model [26] associates an $N \times N$ incidence matrix to a graph of N carbon atoms, whose eigenvalues, E_j, $j \in \{1, \ldots, N\}$ correspond to the discrete energies of independent delocalized π electrons. A closed shell, where half the eigenvalues are negative and half positive (N is even) implies stability (protecting e.g. against Jahn-Teller instability). The largest occupied eigenvalue, $E_{N/2}$, is known as *HOMO*-energy and the smallest unoccupied one, $E_{N/2+1}$, as *LUMO*. A large gap is a criterion for stability. Taking $\frac{1}{N} \sum E_j$ as the reference, $|E_j| \leq 3|\beta|$, where β is the nearest-neighbor overlap integral.

A computer program which calculates the Hückel spectrum for arbitrary g_1, g_2, z and n is available upon request. Illustrative values are summarized in Tables I and II. The average energy per atom is almost insensitive to the number n of unit cells.

The Hückel model also provides an estimate for the electronic charge distribution in the torus. The general trend is that five (resp. seven)-atoms rings capture (resp. release) electrons from/to their adjacent atoms. The

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total capture/release is of the order of a quarter of an electron per ring.

Choice of Examples: The method described above allows to design and analyze infinitely many toroidal molecules. One can for instance require the inner radius of the torus (which is proportional to $nL_{\min}$) to fit the size of a given "guest"; given the mass of a molecule, one could fix $N/n = A$ in Eq. (5); in order to design an elbow that fits a given tubule or cap, one would require a given girth.

The case of two connected concentric cylinders [8] may be reproduced by a two-generation torus with $g_1 \approx g_2 >> z$. Since experimentally found "turn around" edges have a small difference between the external and internal radius (relative to the radii themselves), elongation as in Fig. 10 is necessary. The outer cylinder contains tiles of generation 2, connections contain the zigzagging boundaries, and the inner cylinder contains tiles of generation 1 and separating fringes of generation 2. From geometric arguments and comparison with Eqs. (9) and (10), we estimate g_1 and g_2 as $0.4 \times$ (length of the cylinders), nz as $2.5 \times$ (difference in radii of cylinders) and the total horizontal witdth of the separating fringes as $5 \times$ (the internal radius) minus $2.5 \times$ (the external radius), with all lengths in Å. Note that in this case Eq. (1) is not a good approximation and that interlayer interaction has not been taken into account.

The primitive tori C_{120} and C_{240} in [7] may be traced to be $g_1 = 2$, $g_4 = z = 1$ and the leapfrogged of $g_1 = g_3 = 2$, $z = 1$, respectively. The smallest possible tiling, $g_1 = 2$, $g_2 = z = 1$ is an azulenoid [12].

For the purpose of illustration, we have focused on small values for g_1, g_m and z. Molecules with longitudinal perimeters of the order of that of C_{60} imply girth $g \sim 10$. For tori with roughly circular cross section, we may also expect that the difference in the latitudes of the pentagon and the heptagon lying at the same longitude be at least about $2\pi/3$.

Fig. 14 shows three dimensional views of the two-generations molecule $m = 2$, $g_1 = g_2 = z = 4$ after relaxation to the minimal energy, and Fig. 15 shows $m = 5$, $g_1 = g_5 = 2$, $z = 1$. The latter is the five-generations molecule with the smallest possible indices g_1, g_5 and z. As expected, the five-generations torus is much fatter, and is close to a Clifford torus [19].

Comparison of different levels of inflation of $m = g_1 = g_2 = z = 2$ shows that the configurational energy per atom relative to graphite decreases roughly as $1/N$. (Inflation is the discrete analog of scaling and was discussed in Section 5; inflation by the factor ℓ consists of multiplying g_1, g_m and z by ℓ, and its approximate effect is increase of linear dimensions by this factor.) The same result was obtained in [7]. However, the energy of the least bound atoms saturates. This effect is probably due to the fact that the number of

pentagons and heptagons is kept unchanged, and they bear the entire burden of curvature. In Fig. 14a it is clearly seen that pentagons stick out. It is also interesting to note in Fig. 14b how the pentagons deviate from the latitude $\theta = 0$ which they have in the tiling.

Fig. 16 shows a chiral molecule, obtained by shifting by $j = 1$ the tiling of the molecule in Fig. 15 at $\theta^* = \pi$.

The influence of inflation on the Hückel spectrum was studied for $g_1 = g_2 = 2$ and $1 \leq z \leq 3$. The results are summarized in Figs. 17 and 18. Fig. 17 describes the HOMO-LUMO gap. Since there are N energy levels, and since they are bound in the interval $[3\beta, -3\beta]$, the gap might naively be expected to be inversely proportional to N (and thus to ℓ^2, where ℓ is the inflation factor). The trend is, however, that the gap is inversely proportional to ℓ. This result resembles the case of tubules, where the gap is inversely proportional to the diameter [27]. There are some inflation values for which the regular trend is not obeyed. These are a reminiscent of gap closure for tubules whose width is divisible by 3.

Fig. 18 shows how the delocalisation energy per atom approaches that of graphite. The difference from graphite is, approximately, inversely proportional to ℓ^2.

7   Conclusions

Tori are closed surfaces, like spheres, but unlike spheres are not simply connected. They may provide an arena for a variety of physical and chemical properties.

Table I shows that, from the energetic point of view, there are toroidal molecules with promising stabilities and one could say that the fact that toroidal carbon molecules have not been observed is as significant as the fact that C_{60} molecules were not observed until recently. It is difficult to draw definite conclusions from the comparison of binding energies of molecules that are not isomers. In general, the binding energy per atom increases to the graphite limit as the number of atoms increases and we have found, as in [7], that the total binding energy relative to graphite, $N(\bar{E} - E_G)$, remains roughly constant when the shape of the molecule is kept fixed and the size is increased by means of Goldberg inclusions. $N(\bar{E} - E_G)$ is therefore a representative measure of the price in energy required to form a torus, and is listed in Table I.

The configurational energies and the geometries we have found are similar to those in [7], in spite of having used a different potential and minimization technique. Also, the trend of 5-atom (resp. 7) rings to capture (resp. release) electrons is of the same magnitude as that found in [13]. The Hückel model

predicts that the molecule $g_1 = 2$, $g_4 = z = 1$ (known as C_{120}) has degenerate HOMO-LUMO states; this result disagrees with [13].

We have developed a classification scheme which can be used to "design" toroidal molecules with prescribed dimensions. As long as these molecules are not found, it may help to suggest candidates; if they are found, it may help to sort and analyze them.

Appendix: Choice of Tiles

Not every set of triangles is acceptable for tiling. The tiles must permit a covering of a rectangle with periodic boundary conditions such that adjacent tiles have matching edges. Tiles must also be compatible with vertices with valences 5, 6 and 7. Besides these restrictions, choosing tiles involves some arbitrariness. Our choice was guided by two criteria: geometrical considerations and simplicity. Geometrical considerations should in the end enable us to obtain molecules in which all bonds have approximately the same length

and form angles close to 120°; simplicity will facilitate bookkeeping.

The metric in the tiling plane, Eq. (2), is not Euclidean in $\{\theta, \phi\}$. As a consequence, equal areas in the tiling plane do not correspond to equal areas in the toroidal surface. A unit area in the Euclidean metric of $\{\theta, \phi\}$ for $\theta \sim \pi$ corresponds to a larger area (and, therefore, a larger number of atoms) in the molecule than a unit area for $\theta \sim 0$. Since every tile represents one atom, more tiles cover the latitude for $\theta \sim \pi$ than for $\theta \sim 0$, so that the former tiles must be smaller. We are thus forced by geometry to mind tiles of different sizes; we use simplicity to decree that all tiles be similar. This leaves us with one triangular shape to choose.

Since equilateral triangles are incompatible with valences other than 6 and imply a single tile size, the simplest possibility is that of isosceles triangles. The angles (α, β, β) of the tile must fulfill

$$\alpha + 2\beta = \pi \qquad \text{(A1)}$$

and the valence condition amounts to the three equations

$$n_j \alpha + (j - n_j)\beta = 2\pi, \; j = 5, 6, 7, \qquad \text{(A2)}$$

where j stands for the valence of the vertex and n_j is an integer between 0 and j. Eqs. (A1)-(A2) have exactly three solutions: $(\alpha = \pi/5, n_5 = 0, n_6 = 2, n_7 = 4)$, $(\alpha = \pi/2, n_5 = 3, n_6 = 2, n_7 = 1)$ and $(\alpha = 3\pi/7, n_5 = 4, n_6 = $

$2, n_7 = 0$). We now use the requirement that adjacent tiles have matching edges. Since both sides of α are equal and both sides of β are different, going around a vertex will take us to the same edge only if β is present an even number of times, i. e., $j - n_j$ must be even for all values of j. The only solution that satisfies this requirement is $\alpha = \pi/2$, and we are left with right-angled isosceles triangles as in Fig. 3.

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Table I

m	2	2	2	2	3	4	5	5^1
g_1	2	4	6	2	4	2	2	2
g_m	2	4	6	2	2	1	2	2
z	2	4	6	3	6	1	1	1
g	4	8	12	4	12	6	9	9
N	120	480	1080	180	1200	120	240	240
$\epsilon_h(\beta)$	0.43	0.16	0.08	0.45	0.07	0.04	0.19	0.20
$\epsilon_\ell(\beta)$	-0.27	-0.22	-0.02	-0.18	-0.02	0.04	0.01	-0.04
$10^3(\bar{\epsilon} - \bar{\epsilon}_G)(|\beta|)$	16	4	2	11	2	25	11	9
$10^3(\bar{E} - E_G)/|E_G|$	123	32	16	118	16	76	39	43
$10^3(E_{\text{worst}} - E_G)/|E_G|$	181	114	108	170	115	122	101	100
$N(\bar{E} - E_G)/|E_G|$	14.8	15.6	17.5	21.2	19.5	9.1	9.4	10.4
inner radius (Å)	4.05	8.33	12.57	6.87	14.15	2.02	2.09	2.12
outer radius (Å)	7.29	14.21	21.17	10.14	23.42	6.02	8.49	8.61
height (Å)	2.93	5.68	8.00	3.37	8.13	4.57	6.89	6.96

Table II

\ g_2	1	2	3	1	2	3
z \		$g_1 = 2$			$g_1 = 4$	
1	35	17	22	36	0	1
2	61	70	8	11	51	13
3	71	62	22	44	27	21

Table Captions

Table I Energetic and geometric values for several toroidal molecules, according to Hückel's model and to Tersoff's potential. All the molecules have 5 unit cells. The number of generations m, the girths of the first and last generations g_1 and g_m and the length of a "zig" z determine the tiling. (See paragraph above Eq. (4a).) The second and third columns are inflations of the first. N is the number of atoms in the molecule, $\epsilon_{h,\ell}$ is the energy of the highest occupied (resp. lowest unoccupied) molecular orbital, $\bar{\epsilon}$ is the average energy of delocalized electrons, $\bar{E}$ is the average geometric energy per atom, E_{worst} is the geometric energy associated with the least bound atom, and $\bar{\epsilon}_G = 1.575\beta$ and $E_G = -7.40\text{eV}$ are the delocalisation and the binding energy per atom of an ideal graphitic plane. The molecule in the last column (denoted by $m = 5^1$) is obtained by a chiral shift $j = 1$ of $(m, g_1, g_m, z, n) = (5, 2, 2, 1, 5)$

Table II $10^2 \times (\epsilon_\ell - \epsilon_h)/|\beta|$ for molecules with 2 generations and 5 unit cells, for various values of g_1, g_2 and z.

Figure Captions

Fig. 1 The torus of revolution and its parametrization. The dashed curve C_1 is a circle of radius R in the xy plane, centered at the z axis. Through every point P on the surface of the torus there is a circle C_2 of radius R/η in a plane that contains the z axis; the center of C_2 belongs to C_1. C_2 is a longitudinal line.

Fig. 2 Solid lines and dashed lines describe two graphs, which are duals of each other. Both graphs are in the rectangle $0 \leq \theta, \phi \leq 2\pi$. We shall draw θ (resp. ϕ) as the vertical (resp. horizontal) coordinate. The graph in solid lines has 2 pentagons, 7 hexagons and 2 heptagons. (Periodicity has to be born in mind.) By construction, at every face of a graph that has j edges, its dual has a vertex with valence j (where j edges converge).

Fig. 3 (a) The two tiles of an odd generation. (b) The four tiles of an even generation.

Fig. 4 Even generation tiling with unnecessary crumpling.

Fig. 5 The tiling $m = 4$, $g_1 = 2$, $g_4 = z = 1$. m is the number of generations, g_i is the girth of the i-th generation and z is the number of edges in a zig along the (1,2) interface. Each tile has been marked with the number of its generation. The "X" and the asterisk are centers of inversion. The circle at the center of a third generation tile has been drawn for reference in the text.

For clarity, we have taken a contour that does not cut the tiles (rather than a rectangle); still, the left and the right boundary are identified, i. e., this pattern can be used to cover the plane periodically.

Fig. 6 The tiling $m = g_1 = g_2 = z = 2$.

Fig. 7 The tiling $m = g_1 = g_2 = 2$, $z = 3$. It has the same number of generations and girths as the tiling in Fig. 6, but longer "zig" (and, therefore, longer latitudinal lines).

Fig. 8 Interfaces between regions of tiles with different (necessarily consecutive) generation numbers. (a) Even generation is higher than the odd generation. At the interface, the hypotenuse of an even generation tile matches the cathetus of an odd generation tile. The interface consists, therefore, of oblique lines. (b) Opposite case (odd generation higher than the even generation). The interface is a horizontal line.

Fig. 9 Skeleton of tiling that obeys the 5-6-7 rule and has more than one stripe. (In the figure, $m = 6$ and there are 3 stripes.) The numbers denote the generation of the tiles in the region. g_1, g_m and z determine completely the unit cell of the tiling. The heptagonal vertices of the tiling (not drawn) are at the vertices of the skeleton where generations 1 and 2 (but not 3) meet. Likewise, the pentagonal vertices of the tiling are at the vertices of the skeleton where generations 6 and 5 (but not 4) meet.

Fig. 10 The tiling $g_1 = 2$, $g_2 = z = 1$, after elongation by 1.

Fig. 11 Three unit cells of the tiling $g_1 = g_2 = z_1 = 2$, $z_2 = 1$.

Fig. 12 Unit cell of the tiling $g_1 = 2$, $g_2 = z = 1$, after a Goldberg inclusion with indices $\ell_1 = 1$, $\ell_2 = 2$. The circles indicate the original vertices before the inclusion.

Fig. 13 Tiling of a unit cell of a torus of Ref. [11]. In their notation, this tiling consists of the tubules $L = M = 4$ and $L = 8$, $M = 0$.

Fig. 14 Three-dimensional view of the C_{480} molecule $(m, g_1, g_2, z, n) = (2, 4, 4, 4, 5)$, which minimizes Tersoff's potential. For clarity, only atoms in the foreground are shown. (a) View from "above". (b) Side view.

Fig. 15 Same as Fig. 14, for the C_{240} molecule $(m, g_1, g_5, z, n) = (5, 2, 2, 1, 5)$.

Fig. 16 Same as Fig. 15, but for a chiral isomer of C_{240} with chiral shift $j = 1$.

Fig. 17 Gap in the Hückel spectrum for molecules $(m, g_1, g_2, z, n) = (2, 2\ell, 2\ell, \ell, 5)$, $(2, 2\ell, 2\ell, \ell, 6)$, $(2, 2\ell, 2\ell, 2\ell, 5)$, $(2, 2\ell, 2\ell, 2\ell, 6)$, $(2, 2\ell, 2\ell, 3\ell, 5)$, $(2, 2\ell, 2\ell, 3\ell, 6)$, for $\ell = 1, 2, 3...$ For $z/\ell = 1$ (resp. 2, 3), calculations were carried up to $\ell = 9$ (resp. 8, 5). The numbers in the graph stand for z/ℓ. Calculations for $n = 6$ were carried up to $\ell = 5$; for the values of ℓ for which a number appears only once, the values of the gap for $n = 5$ and $n = 6$ are either identical or indistinguishable within the resolution of the graph. For every z/ℓ, $\ell(\epsilon_\ell - \epsilon_h)$

exhibits approximate periodicity as a function of ℓ, with period 3. Note that the number of atoms in the molecule is proportional to ℓ^2

Fig. 18 Delocalisation energy for the same molecules studied in Fig. 17. $\bar{\epsilon}_G = 1.575\beta$ is the delocalisation energy per atom of an ideal graphitic plane. Again, the ordinates are approximately periodic functions of the inflation factor ℓ.